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BLEACHING AGENT COMPOSITION

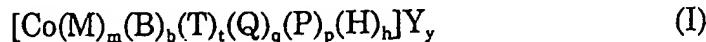
Abstract:

[Object]

This invention provides a bleaching agent composition which shows a good bleaching property and does not cause damage of fibres and decoloration of dyes.

[Means Therefor]

A bleaching agent composition wherein the said composition contains a cobalt compound (I) and the content of hydrogen peroxide or a peroxide which produces hydrogen peroxide in an aqueous solution is less than 0.01% by weight in terms of effective oxygen.

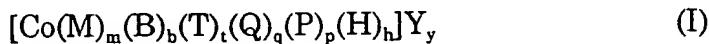


(in the formula, M is a unidentate ligand; B is a bidentate ligand; T is a tridentate ligand; Q is a tetridentate ligand; P is a pentadentate ligand; H is a hexadentate ligand; m is 0-6; b is 0-3; t is 0-2; q is 0-1; p is 0-1; h is 0-1; m +

$2b + 3t + 4q + 5p + 6h = 6$; Y is a counter ion; and y is a number which is necessary for neutralizing the total charge)

We Claim:

1. A bleaching agent composition where the said composition contains a cobalt compound (I) and the content of hydrogen peroxide or a peroxide which produces hydrogen peroxide in an aqueous solution is less than 0.01% by weight in terms of effective oxygen.



(in the formula, M is a unidentate ligand; B is a bidentate ligand; T is a tridentate ligand; Q is a tetridentate ligand; P is a pentadentate ligand; H is a hexadentate ligand; m is 0-6; b is 0-3; t is 0-2; q is 0-1; p is 0-1; h is 0-1; $m + 2b + 3t + 4q + 5p + 6h = 6$; Y is a counter ion; y is a number which is necessary for neutralizing the total charge; and, when M, B and T each is in plural, each ligand may be same or different)

2. The composition according to claim 1, wherein M in the formula (I) contains a ligand represented by NR_3 (where R is a hydrogen atom or is a group selected from a group consisting of an optionally-substituted alkyl group, alkenyl group, cycloalkyl group, aryl group and heterocyclic group and the three R may be same or different) and m is 1-6.
3. The composition according to claim 1, wherein M in the formula (I) contains ammonia and m is 1-6.
4. The composition according to claim 1, wherein B in the formula (I) contains phenanthroline and b is 1-3.
5. A bleaching agent consisting of the cobalt compound represented by the above-mentioned formula (I).

Detailed Description of the Invention:

[Technical Field of the Invention]

The present invention relates to a bleaching agent composition which shows a good bleaching property and does not cause damage of fibres and

decoloration of dyes.

[Prior Art and Problems to be Solved by the Invention]

Use of a peroxy bleaching agent such as hydrogen peroxide in washing is a known art. The peroxy bleaching agent is used at high temperature and is effective for bleaching of tea, coffee, wine and fruit. However, the effect of the peroxy bleaching agent is extremely reduced at 60°C and lower temperature. It has been also and already known that a transition metal ion catalyzes the decomposition of hydrogen peroxide and peroxides which generate hydrogen peroxide such as sodium perborate and sodium percarbonate.

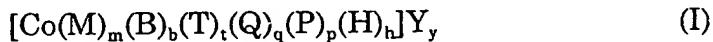
In the Japanese Examined Patent Publication 95/065,074B, there is a disclosure for a method in which a bi-nuclear manganese complex having a nitrogen-containing macrocyclic ligand and hydrogen peroxide or a compound which generates hydrogen peroxide are utilized. A preferred compound as the manganese complex is $Mn^{IV}[\mu\text{-}O_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2]$ but manufacture of such a complicated ligand requires high cost and much time and such a ligand cannot be easily utilized. In addition, there is a problem that a bleaching agent having such a manganese complex damages the fibre and causes the decoloration of dyes.

In U. S. Patent No. 4,810,410, there is a disclosure for a method in which a cobalt amine complex and hydrogen peroxide or a compound which generates hydrogen peroxide are utilized. In that specification, $[Co(NH_3)_5Cl]Cl_2$ is described as a preferred cobalt amine complex but such a cobalt amine complex does not solve the problems of damage of fibres and decoloration of dyes.

In the above-mentioned prior art, it is mentioned that, in order to achieve a good bleaching by the use of such complexes, the presence of hydrogen oxide or a peroxide which generates hydrogen peroxide is essential as an oxidizing agent. However, although that enhances the bleaching power, it is likely that such a thing causes fibre damage and dye discoloration as well. Accordingly, an object of the present invention is to provide a bleaching agent composition which shows a good bleaching property and does not cause damage of fibres and decoloration of dyes.

[Means for Solving the Problems]

The present invention relates to a bleaching agent composition where the said composition contains a cobalt compound (I) and the content of hydrogen peroxide or a peroxide which produces hydrogen peroxide in an aqueous solution is less than 0.01% by weight in terms of effective oxygen.



(in the formula, M is a unidentate ligand; B is a bidentate ligand; T is a tridentate ligand; Q is a tetradentate ligand; P is a pentadentate ligand; H is a hexadentate ligand; m is 0-6; b is 0-3; t is 0-2; q is 0-1; p is 0-1; h is 0-1; m + 2b + 3t + 4q + 5p + 6h = 6; Y is a counter ion; y is a number which is necessary for neutralizing the total charge; and, when M, B and T each is in plural, each ligand may be same or different) and also relates to a bleaching agent consisting of the cobalt compound represented by the said formula (I).

[Best Mode for Carrying Out the Invention]

The cobalt compound of the present invention is represented by the above formula (I) in which examples of the unidentate ligand (M) are a halogen atom such as chlorine, bromine and iodine, a carboxyl group such as acetic acid (*seemingly improper but faithfully translated – translator*); a hydroxyl group, water and NR₃ (where R is a hydrogen atom or selected from a group consisting of an optionally-substituted alkyl group, alkenyl group, cycloalkyl group, aryl group and heterocyclic group and the three R may be same or different); examples of the bidentate ligand (B) are ethylenediamine, o-phenanthroline, 2,2'-dipyridine, 2,2'-dipyrazine, 2,2'-dipiperidine, o-phenylenediamine, 1,2-cyclohexanediamine, 4,4'-dimethyl-2,2'-dipyridine, 2-picollylamine, ethanolamine and glycine; examples of the tridentate ligand (T) are diethylenetriamine, triazacyclononane derivatives such as 1,4,7-trimethyl-1,4,7-triazacyclononane, bis(2-pyridylmethyl)amine, N,N-bis(2-pyridylmethyl)-N-methylamine and iminodiacetic acid; and examples of the tetradentate ligand (Q) are triethylenetetramine, tris(2-pyridylmethyl)amine, nitrilotriacetic acid, derivatives of a saren-type skeleton such as N,N'-di(salicylidene)ethylenediamine, phthalocyanine skeleton derivatives such as 2,9,16,23-tetrasulphophthalocyanine, porphyrin skeleton derivatives such as tetrasulphonated tetraphenylporphyrin and tetraazannulene skeleton derivatives.

Examples of the counter ion (Y) are counter anion which is stable against

oxidation such as Cl^- , Br^- , I^- , NO_3^- , NCS^- , ClO_4^- and OH^- when the charge of the complex as a whole is positive and counter cation such as alkaline metal, alkaline earth metal and alkylammonium salt when the charge of the complex as a whole is negative.

With regard to the cobalt compound represented by the formula (I), the preferred ones are the compounds where M is NR_3 (R has the same meaning as defined already), ammonia or alkylamine such as methylamine (ammonia is particularly preferred) and m is 1-6 and the compounds where B is phenanthroline (hereinafter, abbreviated as "phen") and b is 1-3. To be more specific, they are $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{COO})]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{COO})](\text{NO}_3)_2$, $[\text{Co}(\text{phen})_3]\text{Cl}_3$, etc.

The cobalt compound of the present invention may be made into a preparation by a known method using fatty acid, polyethylene glycol, etc. by conventional extruding granulation, tumbling granulation, etc. It is preferred to use as particles having a particle size of, for example, from about $100\ \mu\text{m}$ to about $1,000\ \mu\text{m}$. The content of the cobalt compound of the formula (I) in the bleaching agent composition of the present invention is preferably 0.0001-5.0% by weight or, more preferably, 0.001-1.0% by weight.

In the bleaching agent composition of the present invention, the content of hydrogen peroxide or a peroxide which generates hydrogen peroxide in an aqueous solution is less than 0.01% by weight as an effective oxygen and, although neither damage of fibres nor decoloration of dyes takes place at that range, the said content is preferably 0%. Incidentally, examples of the peroxide which generates hydrogen peroxide in an aqueous solution are perborates such as sodium perborate, percarbonates such as sodium percarbonate, perphosphates, persulphates and a mixture thereof.

In the present invention, a specific cobalt compound as mentioned above is used whereby, even when the content of hydrogen peroxide or a peroxide which generates hydrogen peroxide in an aqueous solution is less than 0.01% by weight, oxygen which is present as being dissolved in tap water or the like used during the washing acts as an oxidizing agent and, accordingly, a sufficient bleaching property is available and, in addition, significant effect of no fiber damage and no dye discoloration is achieved.

The bleaching agent composition of the present invention may be either powdery or liquid and may contain alkaline agent, surface-active agent,

metal ion sequestering agent, etc. in addition to the above-mentioned essential components. Examples of the alkaline agent are sodium carbonate, potassium carbonate, sodium silicate, sodium bicarbonate, potassium bicarbonate, sodium sulphite, potassium sulphite, sodium sesquicarbonate, sodium orthophosphate, sodium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate.

Examples of the surface-active agent are anionic surface-active agent, nonionic surface-active agent, cationic surface-active agent and amphoteric surface-active agent. Examples of anionic surface-active agent are alkyl benzenesulphonates, alkyl ether sulphates, alkyl sulphates, α -olefinsulfonates, α -sulphofatty acid-ester salts, alkane sulphonates, saturated or unsaturated fatty acid salts, alkyl or alkenyl ether carboxylates, surface-active agents of an amino acid type, surface-active agents of an N-acylamino acid type, alkyl or alkenyl phosphates and salts thereof. Particularly preferred ones are alkyl benzenesulphonates where carbon numbers of the alkyl group are 10-18, alkyl sulphates where carbon numbers of the alkyl group are 10-18 and methyl sodium salt of α -sulphofatty acid where carbon numbers of the fatty acid are 12-18. With regard to a counter ion, preferred ones are sodium, potassium and ammonium and particularly preferred ones are sodium and potassium. Examples of the nonionic surface-active agent are polyoxyalkylenealkyl or alkenyl ethers, polyoxyethylenealkyl phenyl ethers, higher fatty acid alkanolamides or alkylene oxide adducts thereof, sucrose fatty acid esters, alkyl glycosides, fatty acid glycerol monoesters and alkylamine oxides where carbon numbers of the alkyl group or the alkenyl group are 10-18. Examples of the cationic surface-active agent are the surface-active agents of a quaternary ammonium type. Examples of the amphoteric surface-active agent are surface-active agents of a sulphobetaine type and those of a carbobetaine type. Among those surface-active agents, anionic or nonionic ones are particularly preferred. The content of the surface-active agent in the bleaching agent composition of the present invention is preferably not more than 50% by weight or, more preferably, 0.5-40% by weight.

Examples of the metal ion sequestering agent are phosphates such as orthophosphate, pyrophosphate and tripolyphosphate; salts of phosphonic acids such as ethane-1,1-diphosphonic acid and ethane-1,1,2-triphosphonic acid; salts of phosphonocarboxylic acids such as 2-phosphonobutane-2,3,4-tricarboxylic acid and 1-phosphonobutane-2,3,4-tricarboxylic acid; salts of amino acids such as aspartic acid, glutamic acid and glycine;

aminopolysacettes such as nitrilotriacetate, iminodiacetate and ethylenediaminetetraacetate; high-molecular electrolytes such as polyacrylic acid, polyfumaric acid and a copolymer of acrylic acid with maleic acid; salts of organic acids such as diglycolic acid, oxydisuccinic acid, carboxymethyoxysuccinic acid and citric acid (among the salts in that case, alkaline metal salt is suitable); zeolite; and aluminosilicic acid. The content of the metal ion sequestering agent in the bleaching agent composition of the present invention is preferably not more than 30% by weight or, more preferably, 0.1-20% by weight.

The bleaching agent composition of the present invention may further contain re-soiling preventers such as - carboxymethyl cellulose, polyvinylpyrrolidone and polyethylene glycol; fillers such as sodium sulphate; enzymes such as protease, lipase, amylase and cellulase; fluorescent whiteners; dyes; pigments; perfumes; etc.

The bleaching agent composition of the present invention may be added to powdery or liquid detergent for clothing, detergent for hard surface, detergent for dish washer, detergent for artificial tooth, etc. to give bleaching property. The agent may also be used for bleaching agent for hair and also for industrial use such as bleaching of wood pulp. Content of hydrogen peroxide or a peroxide which generates hydrogen peroxide in an aqueous oxygen in the bleaching agent composition of the present invention is less than 0.01% by weight and, therefore, degree of freedom in compounding the bleaching agent composition is improved.

The following experiment was carried out in order to confirm that, in the bleaching agent composition of the present invention, oxygen which is dissolved in water is utilized as an oxidizing agent.

Experimental Example.

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was used as a cobalt compound represented by the formula (I) and coloring of an alkaline solution (4.0×10^{-5} mol/liter) of bilirubin (a model compound for urine-stained dirt) and behaviour of ultraviolet absorption (430 nm) were tested in a system where oxygen was dissolved in (20°C; dissolved oxygen concentration: 8.8 ppm) and a system wherefrom oxygen was removed (dissolved oxygen concentration: 0.14 ppm). The ultraviolet absorption of the system where oxygen was dissolved in to which 10 molar % of a cobalt compound (to bilirubin) lowered with a lapse of time

giving 20% of the initial value after 60 minutes and the color of the solution changed from reddish yellow to pale yellow whereupon bleaching was confirmed. On the other hand, the ultraviolet absorption of the system wherefrom oxygen was removed became 90% of the initial value and no change was noted thereafter. From the results of the above experiments, it was confirmed that bilirubin was bleached by a cobalt compound of the formula (I) using the oxygen dissolved in water as an oxidizing agent.

[Examples]

Unless otherwise mentioned, % in the Examples is that by weight.

Manufacturing Example 1. Manufacture of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Ammonium chloride (8.3 g, 0.155 mol) was dissolved in 50 ml of 28% aqueous ammonia in a 300-ml four-necked round-bottle flask and then 16.7 g (0.07 mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were added whereupon a pale red precipitate was produced. Then 11.4 g (0.117 mol) of 35% hydrogen peroxide were gradually dropped thereinto followed by stirring for 3 hours to give a dark red solution. Into this were dropped 50 ml of concentrated hydrochloric acid during 80 minutes whereupon a reddish purple precipitate was produced. This was heated at 80°C for 15 minutes, cooled and allowed to stand for one night. The precipitate was filtered, washed with cold diluted hydrochloric acid, ethanol and ether and air-dried to give 16 g of the title compound (hereinafter, abbreviated as a cobalt compound B) in reddish purple powdery crystals.

Manufacturing Example 2. Manufacture of $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{COO})]\text{Cl}_2$

Ammonium chloride (25.0 g, 0.467 mol) was dissolved in 150 ml of 28% aqueous ammonia in a 500-ml four-necked round-bottle flask and then 23.8 g (0.10 mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were added whereupon a pale red precipitate was produced. When this was stirred for 1.5 hours, the slurry turned brown colour. Then 34 ml (0.3 mol) of 35% hydrogen peroxide were dropped thereinto during 30 minutes and 30.6 g (0.3 mol) of acetic anhydride were dropped thereinto during 45 minutes followed by stirring for 1 hour at room temperature. The product after completion of the reaction was transferred to a 1000-ml beaker and allowed to stand for one night with 600 ml of isopropanol. The precipitate was filtered, washed with isopropanol and ether and then air-dried to give 20.6 g of the title compound (hereinafter,

abbreviated as a cobalt compound C) in reddish purple powdery crystals (λ_{\max} 502.5, 360 nm).

Manufacturing Example 3. Manufacture of $[\text{Co}(\text{phen})_3]\text{Cl}_3$

Chloropentammine cobalt (III) chloride (4.0 g, 0.016 mol), 9.7 g (0.049 mol) of 1,10-phenanthroline monohydrate, 70 ml of water and 30 g of methanol were placed in a 300-ml four-necked round-bottom flask and heated to reflux for 10 hours. After being cooled, this was concentrated and allowed to stand for one night. The precipitate was filtered, recrystallized from water/ethanol, washed with ethanol and air-dried to give the title compound (hereinafter, abbreviated as a cobalt compound D) in yellow powdery crystals.

Examples 1-10 and Comparative Examples 1-4.

Commercially available $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (hereinafter, abbreviated as a cobalt compound A) and the cobalt compounds B~D manufactured in the Manufacturing Examples 1-3 were used as the cobalt compounds of the present invention together with using the following E and F as surface-active agents and sodium carbonate as an alkaline agent whereupon the bleaching agent compositions of the present invention having the formulations of Table 1 were prepared. In the meanwhile, a bleaching agent compositions for comparison having the formulations of Table 1 were prepared as well. The resulting bleaching agent compositions were evaluated for their bleaching property and decolorizing property by the following methods. The result is given in Table 1.

<Surface-Active Agents>

E: Polyoxyethylene lauryl ether (average molar numbers of ethylene oxide (EO) added were 9)

F: Sodium alkyl (C_{12}) benzenesulphonate

<Method for Evaluating the Bleaching Property>

(1) Preparation of Stained Cloth

Bilirubin (manufactured by Merck) (0.03 g) was dissolved in 100 ml of chloroform and 0.06 ml of the solution was dropped onto a cotton cloth of 8 cm \times 8 cm homogeneously on the cloth followed by drying to prepare a

bilirubin-stained cloth.

(2) Evaluation of Bleaching Property

Deionized water (500 ml) was placed in a one-liter beaker, a bleaching agent composition as shown in Table 1 was added, the mixture was stirred at 100 rpm for 1 minute and five sheets of the stained cloth prepared as above were placed therein, dipped for 30 minutes, washed with water and dried. Concentration of the bleaching agent composition was made 5 g/liter. Reflectance of the resulting stained cloth before bleaching/washing, the stained cloth before bleaching/washing and the original cotton cloth was measured at 460 nm using an NOR-101DP manufactured by Nippon Denshoku Kogyo, the bleaching rate was calculated by the following expression and the bleaching property was evaluated according to the following criteria.

$$\text{Bleaching Rate (\%)} = \{[(\text{Reflectance after Bleaching/Washing}) - (\text{Reflectance before Bleaching/Washing})]/[(\text{Reflectance of Original Cotton}) - (\text{Reflectance before Bleaching/Washing})]\} \times 100$$

Criteria for Evaluating the Bleaching Property

- ×: 10% \leq bleaching rate < 20%
- △: 20% \leq bleaching rate < 30%
- : 30% \leq bleaching rate

<Method for Evaluating the Decolorizing Property>

(1) Preparation of Decolorized Test Cloth

Knitted smooth silkette consisting of 100% cotton was subjected to a dip dyeing with a dye (C.I. Reactive Red 41) to make its concentration in the cloth 4%, then washed with water and subjected to soaping and pressing to give a test cloth of 10 \times 10 cm.

(2) Evaluation of the Decolorizing Property

The bleaching agent composition (10 g) was dissolved in 2 liters of tap water and the test cloth prepared as above was soaked therein for 30 minutes, washed with water, dehydrated and dried. Such a treatment was repeatedly carried out for 20 times and the decolorizing property was

evaluated by naked eye according to the following criteria.

Criteria for Evaluating the Decolorizing Property

- 1: not discolored
- 2: a bit discolored
- 3: discolored
- 4: considerably discolored
- 5: significantly discolored

Table 1

	Examples						
	1	2	3	4	5	6	7
Bleaching Agent Composition (%)							
Co compd A	0.001	0.05	0.5				
Co compd B				0.001	0.05	0.5	
Co compd C							0.001
Co compd D							
Na carbonate	balance	balance	balance	balance	balance	balance	balance
Na percarbonate	0	0	0	0	0	0	0
Surfactant E	2	2	2	2	2	2	
Surfactant F							2
Bleaching Property	○	○	○	○	○	○	○
Decolorizing Property	1	1	1	1	1	1	1

.....continued)	Examples				Comparative Examples			
	8	9	10		1	2	3	4
Bleaching Agent Composition (%)								
Co compd A					0.5			
Co compd B						0.5		
Co compd C	0.05	0.5					0.5	
Co compd D			0.5					
Na carbonate	balance	balance	balance	balance	balance	balance	balance	balance
Na percarbonate	0	0	0	0	80	80	80	
Surfactant E				2	2	2	2	
Surfactant F	2	2	2					
Bleaching Property	○	○	○	×	○	○	○	
Decolorizing Property	1	1	1	1	3	5	4	

Examples 11-16 and Comparative Example 5-7.

To 2 liters of tap water were added 1.33 g of a bleaching agent composition having the formulations shown in Examples and Comparative Examples of Table 2, the mixture was stirred at 25°C and 100 rpm for 1 minute and five sheets of the already-prepared test cloth were placed therein and soaked for 15 minutes. After that, the test cloth was taken out, rinsed with tap water and dried. Bleaching property and decolorizing property were evaluated by the same manner as in Examples 1-10 and the result is shown in Table 2.

Table 2

	Examples					
	11	12	13	14	15	16
Bleaching Agent Composition (%)						
Co compd A	0.1	0.5				
Co compd B			0.1	0.5		
Co compd C					0.1	0.5
Na carbonate	10	10	10	10	10	10
Na percarbonate	0	0	0	0	0	0
Surfactant G *1	25	25			25	25
Surfactant H *1	5	5	3	3	5	5
Surfactant I *1	3	3	25	25	3	3
Surfactant J *1	3	3	3	3	3	3
Zeolite (type A)	10	10	10	10	10	10
Na silicate (#2)	5	5	5	5	5	5
Na polyacrylate *2	5	5	5	5	5	5
Tinopal CBS *3	0.5	0.5	0.5	0.5	0.5	0.5
Protease	0.5	0.5	0.5	0.5	0.5	0.5
Na sulphate	balance	balance	balance	balance	balance	balance
Bleaching Property	○	○	○	○	○	○
Decolorizing Property	1	1	1	1	1	1

(continued.....)

(.....continued)	Comparative Examples		
	5	6	7
Bleaching Agent Composition (%)			
Co compd A	0.5		
Co compd B		0.5	

Co compd C			0.5
Na carbonate	10	10	10
Na percarbonate	10	10	10
Surfactant G *1	25	25	25
Surfactant H *1	5	5	5
Surfactant I *1	3	3	3
Surfactant J *1	3	3	3
Zeolite (type A)	10	10	10
Na silicate (#2)	5	5	5
Na polyacrylate *2	5	5	5
Tinopal CBS *3	0.5	0.5	0.5
Protease	0.5	0.5	0.5
Na sulphate	balance	balance	balance
Bleaching Property	○	○	○
Decolorizing Property	3	3	3

Notes

*1: Surface-active agents

G: polyoxyethylene lauryl ether (av molar nos of ED added = 10)

H: sodium laurylsulphate

I: sodium dodecyl benzenesulphonate

J: fatty acid soap (average carbon atoms: 12; Na salt)

*2: Sodium polyacrylate: (molecular weight = 10,000)

*3: Tinopal CBS: fluorescent whitener (manufactured by Ciba-Geigy)

[End]